Procedures for Detection of Putative Sulfolane Degradation Products in Groundwater

Jan Sunner and Whitney Smith, March 2013

The objective of the analysis is to search for the presence of possible sulfolane degradation products in groundwater. The initial focus will be on smaller sulfur-containing organic compounds. It is expected that a large number of such compounds will be detected (>100) as they are generally present in complex environmental samples. There is, of course, no way to "prove" that any particular identified compound is indeed a sulfolane metabolite from this data alone. Any such identification must be derived from controlled (laboratory) experiments. Rather, the objective is to identify putative metabolites. For this objective it is very important to have the best possible controls, i.e. groundwater samples from outside of any suspected sulfolane "plume".

There are no "out of the box" analytical procedures for the proposed analysis, in particular, since the sulfolane metabolites are not known. Some method development is therefore required. The methods used for this work include sample preparation procedures such as solid-phase extraction followed by GC/MS and LC/MS and extraction of data using dedicated software programs for "feature extraction" and statistical analysis. The LC/MS system is an Agilent 1290 followed by an ultra-high mass resolution Agilent 6538 QToF mass spectrometer. We have previously used this instrumentation extensively for water analysis.

A critical issue for this project is the mode of ionization used for the LC/MS analysis. Our "standard" is electrospray (ESI). In combination with the HPLC and the QToF, it routinely allows for the determination of more than 10,000 compounds in a single (complex) sample. ESI will be our first choice also for the sulfolane analysis. However, we anticipate that likely sulfolane degradation products will have relatively low ionization efficiency in ESI as their basicities are low. This will be an increasing problem as the degradation continues towards mineralization. For such compounds, we have several alternatives, the obvious one being GC/MS with electron ionization. However, we also have access to atmospheric pressure ionization (APCI) and atmospheric pressure photoionization (APPI). Both of these are interfaced to the QToF mass spectrometer. This is important, because of its ability to detect many more compounds and because of its ability to use software to "filter out" sulfur-containing compounds. Finally, Dr Whitney Smith has implemented a method in which low basicity-compounds, such as alkanes, can be made ionizable (by a chemical plasma-induced nitrogen insertion reaction). This method is also interfaced to the QToF mass spectrometer.

SPE Protocol for initial sulfolane studies

1. Remove 3 x 5mL of sample into 3 different clean test tubes
2. Into 1 test tube add 200 µL concentrated phosphoric acid (A); into another test tube, add 200 µL concentrated ammonium hydroxide (B); into the 3rd test tube (N), add nothing.
3. Condition 3 cartridges with 3 mL of methanol and 3 mL of HPLC grade water.
4. Load the samples onto the cartrdiges
5. Wash each cartridge with 4 mL of 5% methanol in HPLC grade water.
6. 2nd washes: For the (A) cartridge: wash with 4 mL of 2% formic acid in 50/50 methanol water For the (B) cartridge: wash with 4 mL of 5% ammonium hydroxide in 50/50 methanol water

For the (N) cartridge, do not apply a second wash.

7. Elution: For the (A) cartridge: elute with 4 mL of 5% ammonium hydroxide in 50/50 methanol water.
For the (B) cartridge: elute with 4 mL of 2% formic acid in 50/50 methanol water
For the (N) cartridge, elute with 4 mL of methanol.
8. Evaporate the elutions to dryness under N2 and reconstitute in 500 µL of 2-propanol.
9. Analyze in positive mode on HILIC and negative mode on RP.

Reversed-phase HPLC QToF procedure for initial sulfolane studies

Column: ACQUITY UPLC® HSS C18 SB 1.8 µm 2.1x100 mm
ZORBAX Eclipse Plus-C18 5µm 2.1x12.5 mm Guard Column
Column Temperature: 40°C
Mobile Phase A: 10% Acetonitrile in HPLC Grade Water
Mobile Phase B: 100% Acetonitrile
Flow rate: 0.4 mL/min

Time (minutes)	% B
0-3	15
3-25	15-95
25-30	95
30-35	95-15
35-40	15

Injection Volume: 5 µL for samples; 20 µL for blanks. 2 Blanks between samples.
QToF Parameters:
Reference Mass Nebulizer: 1 PSI for negative mode
Gas Temperature: 325°C
Drying Gas: 10 L/min
Nebulizer: 40 psig
Vcap: 3500 V
Fragmenter: 160 V
Skimmer: 65 V
OCT 1 RF Vpp: 750 V
Scan Mode 100-2000 m/z
1 spectrum/s
1000 ms/spectrum

HILIC HPLC QToF procedure

Column: ZIC™-HILIC (The Nest Group, Inc.) 150 x 4.6mm, 5µm 200Å
SeQuant ZIC®-HILIC 5µm PEEK 20x2.1mm Guard Column
Column Temperature: 20°C

Mobile Phase A: 5% Acetonitrile in HPLC Grade Water with 0.1% Formic Acid
Mobile Phase B: 100% Acetonitrile with 0.1% Formic Acid
Flow rate: 0.3 mL/min

Time (minutes)	% B
0-30	80-20
30-31	20-5
31-38	5
38-39	5-80
39-46	80

Injection Volume: 5 µL for samples; 20 µL for blanks. 2 Blanks between samples.
QToF Parameters:
Reference Mass Nebulizer: 1 PSI for negative mode
Gas Temperature: 325°C
Drying Gas: 10 L/min
Nebulizer: 40 psig
Vcap: 3500 V
Fragmenter: 160 V
Skimmer: 65 V
OCT 1 RF Vpp: 750 V
Scan Mode 100-2000 m/z
1 spectrum/s
1000 ms/spectrum